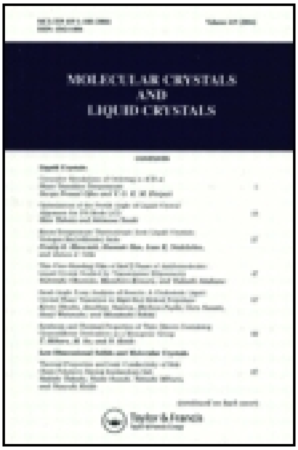

Molecular Crystals and Liquid Crystals

Photochromism of Thienyl-Containing Dihetarylethenes with Five-Membered Cyclic Bridges

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Photochromism of Thienyl-Containing Dihetarylethenes with Five-Membered Cyclic Bridges

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Spectral-kinetic characteristics of a number of new photochromic dihetaryethenes with different five–membered cyclic bridges are measured and discussed. It was shown that these characteristics depend on a bridge structure as well as a nature of substituents in the thienyl fragments.

Keywords: dihetarylethenes; photochromism; spectral and kinetic properties

INTRODUCTION

A primary consideration in the field of modern photochromism is the development of three-dimension bitwise working optical memory. To attain this end the photochromic compounds satisfying to the conditions of this application are required. These compounds must make possible the reversible multiple transformations between initial (A) and photoinduced (B) forms under irradiation exclusively. In this case a thermal relaxation of the photoinduced form is ruled out.

OBJECTS AND EXPERIMENTAL

Among the many photochromic substances which are complying with the requirements, the compounds manifesting the valence isomerization seem to hold the lead [1].

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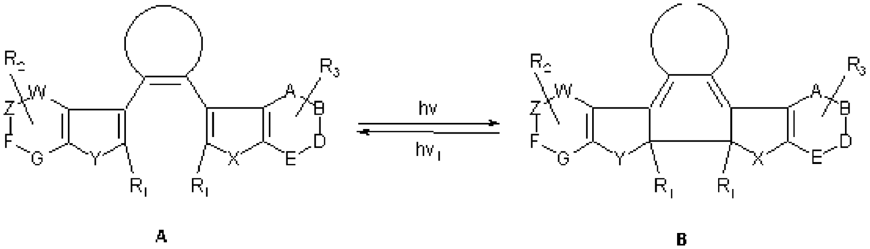
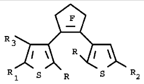
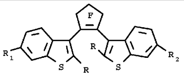
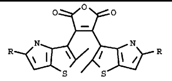
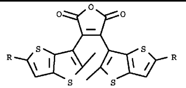
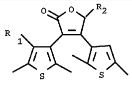
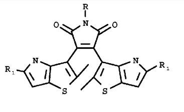
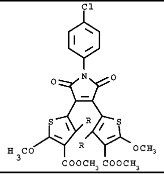
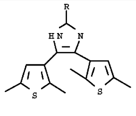
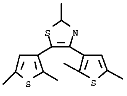
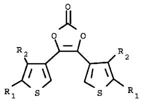
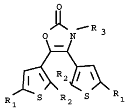
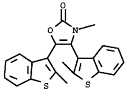


In this paper the comparative study of the spectral and kinetic characteristics for photochromic transformations (Scheme 1) of a number new thienyl-containing dihetarylethenes (DAEs) with the different five-membered cyclic bridges [2] (Table 1) has been carried out.

The spectral and kinetic study was carried out in toluene ($C = 2.10^{-4}$M). Maxima of the absorption spectra of the initial A (λ_A, nm) and photoinduced B (λ_B, nm) forms were measured with the use of the spectrophotometer Cary 50 (Varian) in the spectral range of 200–800 nm. The cyclic form B was prepared by UV irradiation ($\lambda = 313$ nm) of the Hg-lamp (DRSH-250) through the glass UV filter. The photocoloration and photobleaching kinetic curves were obtained at the absorption maximum of the photoinduced form B under UV and visible irradiation separated by the suitable glass filters. From these curves the value of photoinduced optical density ($D^B{}_{max}$) as well as the rate constants for photocoloration (k_{AB}, s^{-1}) and photobleaching

TABLE 1 Structure of the Synthesized Photochromic DAEs

			
Ia (DAE 1-DAE 2)	**Ib** (DAE 10-DAE 13)	**II** (DAEMA 1)	**II** (DAEMA 2)
			
III (L1-L 10)	**IVa** (DAEM I - DAEMI 3)	**IVb** (DAEMI 4,DAEMI 5)	**V** (AZOLE1,AZOLE2)
			
VI (AZOLE 3)	**VII** (CEDAE 1-CEDAE 4)	**VIIIa** (CEDAE 5-CEDAE7)	**VIIIb** (CEDAE 8)

(k_{BA}, s^{-1}) were calculated. The photodegradation curves used by us for comparative appraising recurrence of the photochromic transformations were measured under full irradiation of the above mention lamp. The value of photodegradation was characterized by a decrease of photoinduced optical density for the photostationary state at the absorption maximum of the B form by one half ($T_{0.5degr}$, s). The kinetics of thermal isomerization of this form was obtained by the periodic measuring the absorption spectra with the interval of the several days. Solutions were saved between measurements in the darkness.

RESULTS

It was found that all compounds are characterized by high thermal stability of both forms.

The spectral and kinetic characteristics for the perfluorocyclopentene thienyl (Ia) and benzothienyl (Ib) derivatives are presented in Table 2.

Open forms of all thienyl derivatives absorb in the 285–320 nm range and positions of the absorption maximum don't depend on the molecular structure practically. DAE 1 and DAE 2 are characterized by absorption of the cyclic B form at 535–540 nm. Introduction of the electron-acceptor groups in the thienyl cycles (DAE 3–DAE 5) leads

TABLE 2 Spectral and Kinetic Characteristics of DAEs from the Ia and Ib Groups

DAE	R	R_1	R_2	R_3	λ_A, nm	λ_B, nm	$D^B{}_{max}$	k_{AB}, s^{-1}	k_{BA}, s^{-1}	$T_{0.5phdeg}$, s
1	C_6H_{13}	H	H	H	300	532	0.37	0.18	0.09	120
2	C_2H_5	H_5C_2S	SC_2H_5	H	<300	540	0.77	0.42	0.35	50
3	CH_3	CH_3	$CO(CH_3)$	H	295	580	1.15	0.23	0.11	70
4	CH_3	CH_3	$CO(CH_3)$	HOC	290	565	0.76	0.21	0.09	90
5	CH_3	$(H_3C)OC$	$CO(CH_3)$	H	290	625	1.44	0.21 0.04	0.01	70
6	CH_3	$(H_3C)OC$	CH_2OH	H	290	580	1.40	0.27 0.03	0.08	80
7	CHs_3	$HOCH_2$	CH_2OH	H	300	515	0.98	0.12 0.03	0.05	160
8	CH_3	$HOCH_2$	CH_2O-Py	H	300	520	1.10	0.13 0.02	0.04	190
9	CH_3	Py-OH_2C	CH_2O-Py	H	285	525	0.65	0.14 0.03	0.04	220
10	$CH_2(OCH_3)$	H	H		295	520	0.90	2.40	1.60	160
11	CH_2OCH_3	O_2N	NO_2		340	545	2.00	0.13	0.1	600
12	CH_3	H	$CO(CH_3)$		330	545	1.24	0.21	0.27	480
13	CH_3	$(H_3C)OC$	$CO(CH_3)$		330	555	1.10	0.27	0.28	1040

to the bathochromic shift of the absorption maxima to 580–625 nm. Positions of these bands depend on a number and locations of carbonyl groups. The change of the electron-acceptor groups by electron-donor ones produces the hypsochromic spectral shift (DAE 6 and DAE 7). DAE 3, DAE 5, DAE 6 and DAE 8 have high photocoloration efficiency. The volume substitutes decreases photoinduced optical density. DAE 2, DAE 7–DAE 9 without carbonyl-groups are characterized by low photodegradation.

Open forms of the benzothienyl derivatives (DAE 10-DAE 13) have the absorption bands in more long-wave range as compared with the thienyl derivatives. Influence of the substituent nature is the same as for thienyl diarylethenes. Expect for DAE 11, all compounds of this type are characterized by the acceptable value of photoinduced optical density. High photostability to irreversible photochemical transformations is the most outstanding property of DAE 10–DAE 13.

The absorption maximum for the derivatives of maleic anhydride II may be changed from 510 up to 625 nm according to the nature of the R substituent (Table 3). From the Table 3 we notice that the photodegradation process depends critically on the structure the thienyl fragment.

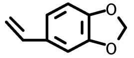
Spectral and kinetic characteristics for lactones (III) depend on the structure of the substituents in the bridge and thienyl fragments (Table 4). L1 and L2 are characterized by the short wave absorption band of the cyclic form with the maximum at 515 nm. Introduction of the carbonyl group into the thinyl fragment leads to increasing light-sensitivity and decreasing fatigue. The electron-donor substituents in the bridge fragment induce the bathochromic spectral shift of the absorption band for the open A and cyclic B forms and, as a rule, decreasing photodegradation efficiency (L3–L8). The nature of the substituent into a phenyl group has the minor effect on the spectral–kinetic characteristics. Introduction of amino–groups into the bridge fragment (L9 and L10) leads to the fast photodegradation of the lactone derivatives.

The maleimide derivatives from the IVa group (DAEMI 1–DAEMI 3) exhibit two absorption bands of the cyclic form at $\lambda_{max} = 420$ and

TABLE 3 Spectral and Kinetic Characteristics of DAEs from the II Group

DAEMA	R	λ_A, nm	λ_B, nm	$D^B{}_{max}$	k_{AB}, s^{-1}	k_{BA}, s^{-1}	$T_{0.5phdeg}$, s
1	$CO(OCH_3)$	295	510	0.48	2.40	0.10	1
2	$CO(OCH_3)$	430	625	2.30	0.07	0.11	400

TABLE 4 Spectral and Kinetic Characteristics of DAEs from the III Group

L	R_1	R_2	λ_A, nm	λ_B, nm	D^B_{max}	k_{AB}, s^{-1}	k_{BA}, s^{-1}	$T_{0,5deg}$, s
1	H	H	300	515	0.35	0.10	0.07	90
2	COH	H	295	515	0.92	0.34	0.19	45
3	H	= –Ph	365	550	0.55	0.68	0.11	120
4	H	= –p–CH_3–Ph	375	550	0.67	0.46	0.10	150
5	H	= –p–Br–Ph	365	550	0.62	0.46	0.11	150
6	H	= –p–OCH_3–Ph	375	550	0.51	1.00	0.12	70
7	H	= –o–OCH_3–Ph	375	550	0.63	0.56	0.17	140
8	H		395	550	0.55	0.68	0.10	70
9	H	= –$N(CH_3)_2$	390	490	–	–	–	50
10	H	= –p–$N(CH_3)_2$–Ph	445	–	–	–	–	500

595 nm (Table 5). Increasing electron-donor capacity of the substituents in the bridge fragment increases the light-sensitivity of the photochromic system. The compounds DAEMI 4 and DAEMI 5 from the IVb group have no photochromic transformations because of the structure of the substituents.

The most short–wavelength absorption maxima of the B form are observed for the derivatives of azoles from the V and VI groups ($\lambda_{max} < 520$ nm) (Table 6) and cyclic ethers from the VII and VIII groups ($\lambda = 425$–455 nm) (Table 7).

Table 6 shows that the compounds from the V group (AZOLE 1, AZOLE 2) are characterized by fast photodegradation. The compound AZOLE 3 has the low light–sensitivity.

It is seen from Table 7 that introduction electron-donor substituent $R_1{=}OCH_3$ into molecules from the VII group (CEDAE 2, CEDAE 3) shifts the absorption maximum of the cyclic form to the long–wave spectral region as compared with unsubstituted compound (CEDAE 1).

TABLE 5 Spectral and Kinetic Characteristics of DAEs from IVa and IVb Groups

DAEMI	R	R_1	λ_A, nm	λ_B, nm	D^B_{max}	k_{AB}, s^{-1}	k_{BA}, s^{-1}	$T_{0,5deg}$, S
1	CH_3	$CO(OCH_3)$	290	420,595	0.65	1.20	0.10	32
2	CH_2–Ph	$CO(OCH_3)$	290	420,595	2.00	1.00	0.15	48
3	CH_2–(CO)Ph	$CO(OCH_3)$	290	420,595	2.40	1.00	0.20	45
4	OH	–	245,290,390,470		No photochromic			
5	$O(CH_2)COOEt$	–	235,280,435		No photochromic			

TABLE 6 Spectral and Kinetic Characteristics of DAEs from V and VI Groups

AZOLE	R	λ_A, nm	λ_B, nm	$D^B{}_{max}$	k_{AB}, s^{-1}	k_{BA}, s^{-1}	$T_{0,5deg}$, s
1	$2{-}Cl{-}C_6H_4$	240,300	>350 (sh)	Fast degradation			28
2	$p{-}C_6H_{13}$	210,230,280	>350 (sh)	Fast degradation			20
3	–	300	515	0.30	0.08	0.11	105

TABLE 7 Spectral and Kinetic Characteristics of DAEs from VII and VIII Groups

CEDAE	R_1	R_2	R_3	λ_A, nm	λ_B, nm	$D^B{}_{max}$	k_{AB}, s^{-1}	k_{BA}, s^{-1}	$T_{0,5deg}$, s
1	H	H		295	425	0.18	0.12	0.09	90
2	OCH_3	–Cl		<300	445	0.33	0.10	0.04	70
3	OCH_3	$COCH_3$		<300	455	0.22	0.18	0.06	70
4	Br	H		250	300,345,400	No photochromic properties			
5	H	H	CH_3	300	430	0.19	0.21	0.13	32
6	CH_3	CH_3	–Ph	300	450	0.17	0.16	1.20	1.5
7	CH_3	CH_3	CH_3	290	455	0.40	0.07	0.02	90
8	–	–	–	<300	455	1.20	0.75	0.45	20

The electron-acceptor group leads to the loss of the photochromic properties (CEDAE 4). The same effect is observed for the photochromic compounds from the VIIIa group (CEDAE 5–CEDAE 7). The bensothienyl derivative VIIIb (CEDAE 8) is characterized by most light-sensitivity as well as the rate constants for photocoloration and photobleaching processes.

CONCLUSIONS

The kinetic and spectral characteristics of dihetarylethenes with the five-membered cyclic bridges may be controlled by changing the bridge structure and nature of the substituents $R{-}R_3$.

The best kinetic characteristics for the photocyclization and photorecyclization processes as well as low photodegradation were measured for the derivatives of perfluorocyclopentene, maleic anhydride and maleimide.

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